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FUNDAMENTALS OF THE OXIDATION
PROTECTION OF
COLUMBIUM AND TANTALUM

By

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Foreword

This is the third semiannual report on NASA Grant No. NGR 33-013-017. It covers work from October 1, 1966 to April 1, 1967.

The first two reports were issued March 31, 1966 and October 1, 1966. Since their distribution was limited, this report contains a comprehensive review of the entire program.

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Summary

An investigation of the fundamental processes involved in the protection of tantalum and columbium by their silicides is in progress. The program has four parts. The first part is devoted to establishing thermochemical data for the silicides and employs an entirely solid state electrochemical cell. The second part deals with the protection of both coating and substrate by the protective glass formed during oxidation. Under certain conditions of temperature and pressure this glass does not form and the coating fails. The study of glass structure and growth is aimed at understanding the causes of failure and providing a rational basis for improving coatings. In the third part oxidation rates and the possibility of using coating modifiers to promote the formation of glassy films is to be tested. Lastly, since coating life may be limited by the formation of intermediate phases between the silicide and the substrate, these interactions are being investigated in the fourth part of the program along with the efficacy of diffusion barriers to retard intermediate phase growth.

In all cases the silicides, with any required additives, will be used in bulk form. Disks are fabricated by cold pressing and sintering. These methods have been developed, and specimens of over 90% theoretical density have been consistently obtained.

The work thus far has been devoted mainly to the development of specimen fabrication techniques, the design and construction of equipment and preliminary tests of some of the methods to be used. This report describes background and methods in detail together with some preliminary results. Plans for the future are also discussed.

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Introduction

Refractory metals are required for a variety of applications at elevated temperatures, particularly for air-breathing engines, because their high strength is retained under service conditions. These metals, however, suffer from a susceptibility to oxidation. Above about 1300[°]F oxidation rates are prohibitive, and a protective coating is required. Silicide and aluminide coatings have been most successful thus far.

The development of coatings has proceeded by largely empirical methods. While this is undoubtedly the way to obtain practical coating systems rapidly, a successful coating technology must be backed by fundamental information on atmosphere-coating-substrate systems.

Previous studies on the development of protective silicide coatings for tantalum and columbium and their alloys at temperatures up to 2500[°]F (1371[°]C) have been carried out at Solar(1-4), Vitro(5), General Telephone and Electronics(6-7) (GT&E), Sylcor(8), and Thompson-Ramo-Woodridge(9) (TRW). In these studies, the coatings were applied to the metal substrate by either pack cementation (Solar), slurry (Sylcor) or electrophoretic (Vitro) techniques. The coated specimens were then subjected to oxidizing conditions to determine the extent to which the coatings were protective to the metal substrate. In most cases, protectiveness was determined by weight gains and visual appearance. In others, an attempt was made to identify the components in the oxide film(6,7,9).

The simplest coating system is obtained by straight siliciding of tantalum or columbium metal. It has been found, however, that TaSi₂ and CbSi₂ form a non-protective oxide scale(3). For this reason, other materials are added to the silicon powder during the coating preparation to improve the oxidation resistance. Some of the materials which give favorable results when used by themselves or in combination with each other are silicides of titanium, chromium, vanadium and molybdenum.

In a fundamental study aimed at determining the composition of the oxide film formed during oxidation of silicide coatings on tantalum carried out by GT&E(7), two coating systems and two metal substrates were used. Straight siliciding and siliciding with 90Ti-10W in the pack were used on tantalum and T-222 alloy ($\sim 88\text{Ta} \cdot 2.7\text{Hf} \cdot 9\text{W}$). The oxide films were studied by x-ray diffraction and electron microprobe analysis.

When the samples that were straight silicided were oxidized, the major oxidation product was found to be Ta_2O_5 . At oxidation temperatures of 2800°F (1538°C) α - Ta_2O_5 predominated, while at 2500°F (1371°C) the β - Ta_2O_5 form was the major product. SiO_2 (α -cristobalite) was present in trace amounts when the tantalum-based silicide coating was oxidized at 2800°F (1538°C), while none was found when T-222 samples were similarly treated. Some shifts were noted in the reflectance peaks of Ta_2O_5 which may indicate SiO_2 solution since thermodynamically SiO_2 should be present.

A somewhat different situation resulted in the case where the Ti-W-Si coating system was used. TiO_2 (rutile) and SiO_2 (α -cristobalite) were the major oxide phases formed at 2500°F (1371°C). Tantalum oxides were not found. As in the straight tantalum work, no SiO_2 was found in the 2800°F (1538°C) samples, TiO_2 (rutile) being the main product. In this case, the lack of indication of SiO_2 may be caused by its amorphous state while suffering interference from the strong orientation in the TiO_2 reflections.

Somewhat more information is available on the oxide formed on silicide coatings on columbium alloys. In a study similar to that described for the tantalum system, also carried out at GT&E(7), the oxide was analyzed using X-ray and electron diffraction. For the case where titanium was used as an additive prior to the siliciding, TiO_2 (rutile) and SiO_2 (α -cristobalite) were formed. In addition, $\text{TiO}_2 \cdot \text{Cb}_2\text{O}_5$ was also indicated as a possible product. When chromium was added to the

silicide coating, CrCbO_4 was formed and weight change data indicated ion mobility was lower in this than in a film containing a mixture of SiO_2 and Cb_2O_5 . In both the tantalum and columbium studies, the weight gain measurements indicated either parabolic and/or linear kinetics.

A fundamental study on the oxidation of bulk molybdenum disilicide (MoSi_2) was carried out at Aeroneutronic(10). This study is of interest because it is one of the few cases where the oxide film on a bulk disilicide has been studied in detail. Analytical techniques similar to those used at GT&E were applied. The mechanism for MoSi_2 oxidation is different from that of TaSi_2 and CbSi_2 because the oxide MoO_3 , is volatile. Therefore, at temperatures of 2200°F (1240°C), the major oxide present was found to be almost entirely amorphous SiO_2 with only small islands of MoO_3 . At lower temperatures, more MoO_3 was present in the film resulting in poorer protection.

Samsonov reports data on the oxidation of pure titanium disilicide (TiSi_2) which indicates that it has superior oxidation resistance(26). A specimen of pure TiSi_2 oxidized in air at 2192°F (1200°C) for four hours had a weight gain of only 0.3 mg/cm^2 . This protectiveness is attributed by Samsonov to the formation of a tenaciously bonded vitreous film consisting of a eutectic mixture of titanium silicates.

The program described here has been undertaken to provide an understanding of the behavior of the coated substrate in its environment. This involves the mechanisms and rates of oxidation of the coating and the effects of modifiers as well as the mechanisms and rates of interaction of the coating with the substrate. The tantalum-silicon and columbium-silicon systems, at temperatures up to 2500°F and under oxygen pressures of one atmosphere and above, are under study.

Four major lines of investigation are in progress:

- 1) thermochemical data,
- 2) glass structure and growth,
- 3) oxidation rates and coating modifiers
- 4) substrate-coating interaction and barriers.

To discuss the behavior of tantalum-silicon and columbium-silicon systems under oxidation requires thermochemical data for the oxides and silicides. At present the free energies of formation of the silicides of tantalum and columbium are not available. These will be determined in the first part of the program using a solid galvanic cell at elevated temperature.

The oxidation protection of metals by silicides depends on the formation during oxidation of a glass which acts as a barrier to oxygen. As noted in literature review above, the oxidation products frequently do not form a protective film. In the second line of investigation the glasses formed on oxidation are being investigated with the objective of understanding the differences between the structure of protective and nonprotective films and the processes controlling their growth. This understanding will provide a rational basis for improving the protectiveness of coatings.

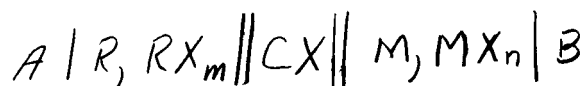
The possibility of using modifiers to improve the structure of the film is being investigated in the third part of this program. Substances which form stable oxides or silicates may be expected to increase coating life and a number of these will be tested.

In the fourth phase of the project the interaction of the coating with the substrate is being studied. This interaction produces an intermediate silicide incapable of forming a protective film. The rate of growth of the intermediate phase may thus determine coating life. These phases grow by diffusion, and the use of barriers to slow the growth of the intermediate has been reported.

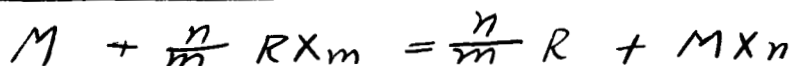
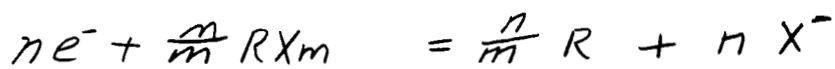
Thermochemical Data

Presently available thermodynamic data for tantalum and columbium silicides are limited to heats of formation obtained calorimetrically (Robins and Jenkins (30)), by Knudsen effusion (Myers and Searcy(31)), or by reaction equilibria (Brewer and Krikorian(32)). The average accuracy of the best available data is about $\pm 15\%$. To date there have been no experimental determinations of the free energy and entropy of formation of these silicides. The free energy of formation of these compounds can only be estimated from heat of formation data under the assumption of a zero entropy of formation.

Thermodynamic investigations of metal non-metal compounds have followed three well established directions. The first is calorimetric determination of the heat of formation of the compound coupled with entropy of formation data obtained through the Third Law. A second technique is based on gas-solid equilibria: the free energy of formation is determined either from dissociation equilibria or, where applicable, from reduction equilibria. A third technique which has recently come into prominence as a result of the work of Kiukkola and Wagner(33) is based on the measurement of the EMF produced by an electrochemical cell. In this method a reference electrode is separated from an electrode composed of the system of interest by a solid electrolyte. In most instances the electrolyte conducts by anion migration, although several cells based on cationic electrolytes have been formulated and operated successfully. A general formulation for these cells is:



where CX is the electrolyte (in this case an anionic conductor); R, RX_m is the reference electrode; M, MX_n is the system under study, and A and B are the electrical lead materials. The EMF of the above cell, after correction for the thermoelectric EMF, is related to the free energy of the cell reaction:



(1)

by

$$\Delta G_R = -n F E$$

(2)

provided that the following conditions are met within the cell:

- 1) The cell reaction is reversible.
- 2) No other reactions occur within the cell.
- 3) Electrical conduction occurs solely as a result of the cell reaction; that is, the electrolyte is a pure ionic conductor.

From equations (1) and (2) the free energy of formation of MX_n is:

$$G_{MX_n} = \frac{n}{m} G_{RX_m} - n F E \quad (3)$$

The entropy of formation of MX_n is determined from the temperature dependence of the EMF:

$$S_{MX_n} = \frac{n}{m} S_{RX_m} + n F \frac{dE}{dT} \quad (4)$$

Among the systems which have been successfully studied by means of electrochemical cells employing solid electrolytes are metal oxides, sulfides, halides and carbides. The majority of the systems studied involved metal oxides. This is due to the availability of a number of inert ceramic oxide electrolytes about which there is a large body of information. The most common oxide electrolytes are based on either thorium, zirconia or hafnia. These oxides are doped with a second oxide to create a well defined number of oxygen ion vacancies. Vacancies enhance the ionic conductivity of the electrolyte and thereby facilitate EMF measurements. Common doping agents are magnesia, calcia, yttria

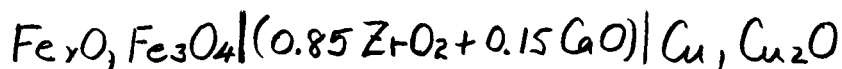
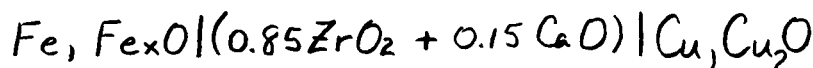
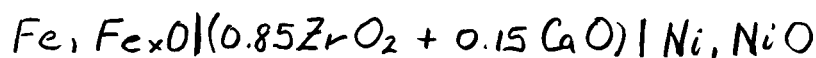
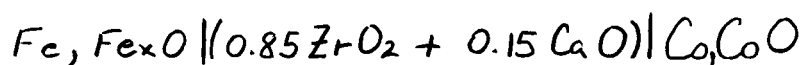
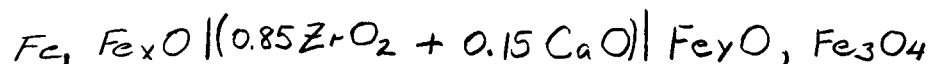
and lanthana. The cation of the doping agent occupies cation sites otherwise filled by those of the primary oxide. The number of oxygen ion vacancies created per mole of the doping agent depends on the valence of the doping cation. Bivalent cation additives create one mole of anion vacancies per mole of additive while trivalent cation additives create 1/2 mole of anion vacancies per mole of additive.

There are a large number of contributors to the literature dealing with solid-state oxide electrolytes. Among the investigators of electrical conductivity and transport number are Kiukkola and Wagner(33) who studied conductivity in ZrO_2CaO as a function of oxygen partial pressure. Steele and Alcock(34) determined electrical conductivity in the thoria-yttria, thoria-lanthana and thoria-calcia as a function of temperature, pressure and composition. Vest and Tallan(35) investigated the electrical conductivity of ZrO_2CaO using a polarization technique while Kingery(36) studied oxygen ion mobility. Johansen and Cleary(37) investigated the high-temperature electrical conductivity of ZrO_2CaO and HfO_2CaO solid solutions. Additional work on oxide electrolytes was conducted by Bray and Merten(38), Strickler and Carlson(39) and many others.

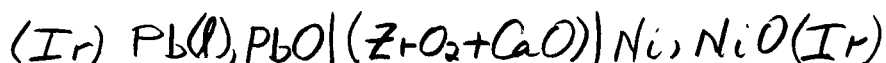
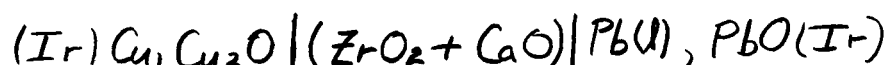
From these investigations the following generalizations may be made with regard to binary solid-state oxide electrolytes. The log of the ionic conductivity is directly proportional to the anionic vacancy concentration at low concentrations. The conductivity reaches a maximum between 6 and 15 atom % of the additive depending on the nature of the host lattice and the size of the added cation. Smaller cationic additives enhance the conductivity of the host lattice more effectively than larger cationic additives. Over the range of oxygen partial pressures where ionic conduction prevails, the electrical conductivity is not a function of oxygen partial pressure. At higher oxygen pressures electronic conduction by electron holes accompanies ionic conduction while at lower oxygen pressures, n-type electronic conduction occurs in conjunction with ionic conduction. The electronic components are

a function of oxygen partial pressure. The temperature dependence of the ionic conductivity is given by an Arrhenius expression.

There have been many thermodynamic studies conducted with oxide electrolytes of which a few will be mentioned. Kiukkola and Wagner(33) studied the following cells:

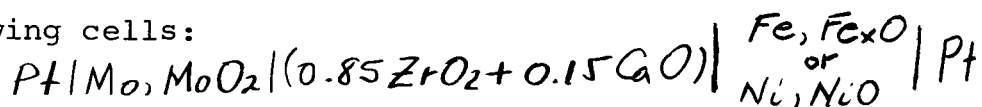


Steele and Alcock(34), in addition to replicating some of the cells investigated by Kiukkola and Wagner, studied the following systems:



as well as the systems Nb - NbO, NbO - NbO₂ and NbO₂ - Nb₂O₅ with respect to Fe - Fe_xO and Ni - NiO and with respect to each other using zirconia and thorium based electrolytes. Electrolytes based on zirconia exhibited electronic conduction at the low oxygen partial present in the latter experiments.

Rapp(40) determined the free energy of formation of MoO₂ from the following cells:

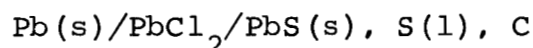
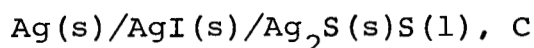


Rapp in collaboration with Maak(41) investigated the thermodynamic properties of solid copper-nickel alloys using the cell

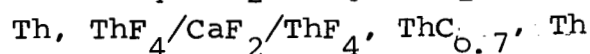
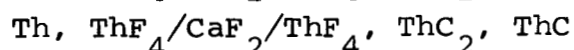
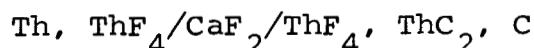


Matsushita and Goto(43) used zirconia-calcia to repeat some former work and added SnO , PbO , CaO and Ta_2O_5 to the list of oxides studied. Worrell(44) investigated the stabilities of tantalum and columbium oxides using thoria-yttria and thoria-calcia electrolytes. The investigations made with tantalum and columbium oxides are of particular interest since these materials exert low oxygen partial pressures at which appreciable electronic conduction is expected for zirconia-calcia and near the expected limit for thoria-yttria. The success of some of these experiments points out the wide divergence of opinion surrounding this matter.

Among the thermodynamic studies performed with non-oxide electrolytes are those of Kiukkola and Wagner(43) employing the cells:



Aronson(45) investigated thorium carbides using a calcium fluoride electrolyte in the following cells:



Similar cells were used by Aronson and Auskern(46) to study thorium borides.

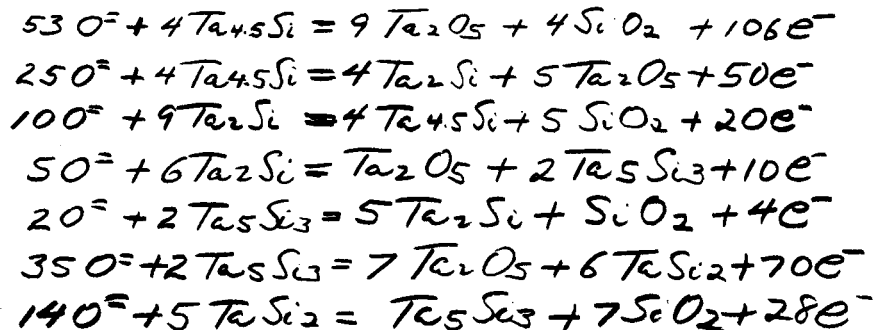
Method:

Free energies of formation of refractory metal silicides are to be determined with electrochemical cells employing solid electrolytes. The technique will first be applied to the tantalum-silicon system and will later be applied to columbium and other refractory metal silicides. Initial studies employ oxide electrolytes, thoria doped with 10 to 12 mole % yttria being the most promising. An intimate mixture of nickel and nickel oxide serves as the reference electrode.

In the absence of a complete set of ternary phase diagrams the silicide electrode must be formulated from the tantalum - silicon phase diagram(37) and the available data on heats of formation of tantalum silicides. The proper series of electrodes appears to be intimate equilibrated mixtures of $Ta_{4.5}Si - Ta_2O_5 - SiO_2$; $Ta_{4.5}Si - Ta_2Si - SiO_2$; $Ta_{4.5}Si - Ta_2Si - Ta_2O_5$; $Ta_2Si - Ta_5Si_3 - Ta_2O_5$; $Ta_2Si - Ta_5Si_3 - SiO_2$; $Ta_5Si_3 - TaSi_2 - SiO_2$ and $Ta_5Si_3 - TaSi_2 - Ta_2O_5$. Measurements on this series with already available free energy of formation of Ta_2O_5 , SiO_2 and NiO will give the free energies of formation of the tantalum silicides. The reference electrode half-cell reaction is:



The expected reactions at the silicide electrodes are:



EMF measurements on the galvanic cells will be made in the temperature range $900^{\circ}F$ to $2200^{\circ}F$ (about $500^{\circ}C$ to $1200^{\circ}C$) in inert atmosphere. Most of the cell voltage is bucked by a potentiometer and the remaining voltage is measured with an electrometer. The apparatus is shown in Figure 1 with measurement and control apparatus, power supplies, and gas train indicated schematically. Temperature is measured and controlled to within $\pm 3^{\circ}$. The EMF is measured to the nearest millivolt. Argon is dried with anhydrous magnesium perchlorate and deoxidized with either copper or zirconium - titanium alloy. The cell is loaded between fused quartz rods housed in a Vycor or fused quartz cylinder. The load is applied through a Veeco coupling. This arrangement provides considerable flexibility in going to more sophisticated designs. Brass end flanges with o-ring seals close off the

system. Electrical access to the cell is provided by vacuum lead-throughs.

Preliminary Results

Preliminary studies were made with zirconia-7.5 wt. per cent calcia and thoria - 15 wt. per cent yttria electrolytes. The first system investigated was Cu, Cu_2O against Ni, NiO with a zirconia-calcia electrolyte. Results agreed with those obtained by Steele and Alcock(34) to within 1% at 600, 700 and 800°C. The cell Ni, NiO/ ZrO_2 CaO/ TaSi_2 , SiO_2 gave no steady EMF. After 15 minutes of operation the EMF of the cell was 620 mv. The EMF decreased steadily to 23 mv at 18 hours. The cell was then operated at 500, 600 and 800°C for one hour periods. The EMF was extremely sensitive to this temperature variation; the values observed were 769, 230 and 146 mv respectively. Substitution of thoria-yttria did not result in a stable EMF at 700°C. The EMF increased from 275 mv after 84 minutes of operation to 511 mv after 21 hours and was sensitive to the argon flow rate.

The cell Ni, NiO/(Electrolyte)/Ta, TaSi_2 , SiO_2 was run with ZrO_2 ·CaO and ThO_2 · Y_2O_3 . The former electrolyte gave EMFs of 307, 313 and 316 at 600, 700 and 800°C while the latter gave a value of 530 mv at 700°C.

Ta, Ta_2O_5 and Si, SiO_2 electrodes were tested against Ni, NiO with zirconia-calcia as the electrolyte. The Ta, Ta_2O_5 electrode gave erroneous values due to poor cell alignment. A value in agreement with Matsushita and Goto(43) was obtained for a short time. The Si, SiO_2 electrode gave no meaningful voltage.

The final cell tested was Ni, NiO/(ThO_2 · Y_2O_3)/ TaSi_2 , Ta_5Si_3 , SiO_2 . Steady values of the EMF were obtained. These values were not reproducible on thermal cycling.

The difficulties encountered in the preliminary experiments may be summarized as follows: poorly established contacts at the electrode - electrolyte interface, reaction of the platinum lead with the silicide

electrodes and an excessive oxygen partial pressure in the argon used. These difficulties prevented positive identification of the sources of the observed EMFs. For the next series of experiments an apparatus has been constructed using a gas purification train; positive loading of the assembled cell and a silicide contact at the silicide electrode. This improved apparatus is now being tested.

Electrode Synthesis and X-Ray Studies

Ni - NiO, Ta - (β)Ta₂O₅ and Cu - Cu₂O reference electrodes were fabricated in wafer form. The composition of the silicide electrodes and their locations in the appropriate phase fields are shown in Figure 2. These electrodes were prepared by first reacting in vacuum elemental tantalum and silicon in the appropriate proportions in wafer form. The products were examined by X-ray diffraction. In all cases the expected silicides were detected as well as trace amounts of neighboring phases. The reacted pellets were then ground and β -quartz or β -tantalum oxide added. These powders were mixed, pelletized and heat treated for 10 minutes at approximately 1350°C and 2×10^{-4} Torr. X-ray diffraction analysis was again performed. The expected silicides were again detected along with possible traces of neighboring silicide phases.

To determine whether tantalum forms a silicate, β -tantalum oxide and β -quartz were mixed and heated in pellet form for 32 hours at 1200°C. X-ray diffraction analysis did not detect the presence of a third phase.

There is some uncertainty about the lowest silicide. Samsonov(22) reports that Ta_{4.5}-Si may be the lowest silicide. Aronson et al(48) report Ta₃Si as the lowest silicide with Ta_{4.5}Si being favored when stabilizing impurities such as carbon and aluminum are present. Resolution of this question is necessary to carry out the measurement scheme.

In order to determine the nature of the lowest silicide in the tantalum-silicon system a phase study was conducted. The locations of

the compositions studied with respect to the phase boundaries are indicated in the upper portion of Figure 2. The materials were prepared from elemental tantalum and silicon reacted in vacuum in pellet form. The products were ground to powder, pelletized and heat treated for ten minutes at approximately 1600°C (2912°F) and 2×10^{-4} Torr. X-ray diffraction analysis indicated that A (Fig. 2) contained approximately equal quantities of Ta_2Si and Ta_5Si_3 with a trace of Ta_xSi ; B contained approximately equal quantities of Ta_xSi and Ta_2Si with a trace of Ta_α ; C consisted of principally Ta_xSi with an appreciable amount of Ta_2Si and a trace of Ta_α ; D consisted principally of Ta_xSi with appreciable Ta_2Si and Ta_α while E contained approximately equal quantities of Ta_α and Ta_xSi . This indicates that $\text{Ta}_{4.5}\text{Si}$ is being produced rather than Ta_3Si and that the former will be the silicide present in the electrochemical cell.

Glass Structure and Growth

All of the current and previous fundamental studies on the oxidation characteristics of tantalum and columbium disilicides, as noted in the above literature review, have been performed on the disilicide diffusion bonded to the metal substrate. In these studies, interaction of the substrate with the coating and physical character of the coating itself obscures the intrinsic oxidation resistance of the coating material. In many cases, examination of a cross section of the sample indicates the presence of large and small cracks. Oxidation in these cracks results in rapid failure of the specimen. In addition, a large difference in thermal expansion of the coating and substrate can result in failure.

In order to clearly establish the intrinsic oxidation behavior of the coating materials, their oxidation is being studied in bulk form. This approach to the coating problem is particularly attractive in that it eliminates the physical problems found in coatings, and also allows the effects of small amounts of additives to be determined.

In order to study the character of the protective oxide film that is desired in coating applications, it is necessary to add other materials to TaSi_2 since, as indicated earlier, the pure material does not form a protective film. Because titanium is found in some of the promising coatings for tantalum, the Ti-Ta-Si system was chosen for study. The study includes the oxidation of pure TiSi_2 , $\text{TiSi}_2 + \text{Si}$, $\text{TaSi}_2 + \text{Si}$ and $\text{TaSi}_2 + \text{TiSi}_2$. If suitable samples can be prepared, Ta_5Si_3 and Ti_5Si_3 will also be considered. Since TiSi_2 is the major component in coatings for columbium alloys also, the study can easily be extended to cover that system.

The phase diagrams for the mixtures of interest are shown in Figures 3, 4 and 5. Figures 3 and 4 for the TaSi_2 -Si and TiSi_2 -Si systems indicate that only the pure material phases are present below the eutectic temperature ($\sim 1400^\circ\text{C}$ (2550°F) for Ta and 1330°C (2435°F))

for Ti). Therefore, the effect of excess free silicon in the coating material can be readily established.

For the TaSi_2 - TiSi_2 , Figure 5 shows that a terminal solid solution containing a maximum of approximately 50 percent TiSi_2 is formed. Below this composition a single solid solution exists, while at higher TiSi_2 contents, two phases are present: pure TiSi_2 and the solid solution. Samples above and below the 50 percent composition will be tested to determine whether the presence of the two phases affects the oxidation reaction.

Sample Preparation

Wafers of the material to be studied are prepared using the techniques of powder metallurgy. In this method, the powders of the materials of interest are mixed with approximately 0.5 weight percent binder, cold pressed in a die at pressures of 2-5 tsi and sintered. A satisfactory procedure using this general approach has been developed here and is as follows:

Polymethylmethacrylate dissolved in methyl ethyl ketone is found to be a satisfactory binder. The pressed wafer is presintered in vacuum to about 1652°F (900°C) to remove the binder and then sintered again to achieve the desired density. The final sintering temperature depends on the material being sintered; usually 70-90 percent of the absolute melting temperature is adequate. Sintered samples are then ground and polished. Samples of pure TiSi_2 prepared in this manner have approximately 95 percent of the theoretical density. Samples of the final polished wafers are ground and analyzed by X-ray diffraction to verify that no changes in composition have occurred. This is followed by sectioning, etching and metallographic examination.

Oxidation of the polished wafers is initially being carried out in atmospheric air in a box-type furnace. In later studies, a controlled atmosphere will be used in either a box or tube-type furnace.

Oxygen partial pressures of one atmosphere and more, and temperatures of up to 2400°F (1316°C) will be studied.

Analytical Methods

In order to elucidate the mechanism associated with the oxide growth, the overall weight change, composition and thickness of the oxide film will be determined as a function of time of oxidation, temperature, oxygen pressure and substrate composition. In the determination of the composition of the oxide film, X-ray diffraction and infrared spectroscopy will be used. The X-ray diffraction studies will be carried out using the standard powder technique. The characteristic lines obtained will be identified by comparison with the ASTM Data Card File and also with suitable standards. The results should indicate the crystalline materials present and also their isomorphic form.

In order to use the X-ray diffraction technique, part or all of the substrate material must be separated from the film. A technique that has proven successful in silicon technology(14) consists in removing a small part of the oxide film down to the silicon substrate with HF and then placing the sample in dry chlorine at $932-1652^{\circ}\text{F}$ ($500-900^{\circ}\text{C}$). Silicon tetrachloride forms and is removed as a vapor, leaving a hole in the silicon through to the oxide film on the opposite side. Studies at Aeroneutronic(10) indicate a successful reaction with chlorine and MoSi_2 to separate the oxide film. It is anticipated that this technique may be used with the materials being considered here since they all form volatile chlorides, and it has been shown that TiO_2 is not attacked by chlorine(15), and while Ta_2O_5 apparently reacts with chlorine, the conditions may be altered to eliminate the reaction. Initially, the X-ray beam will be directed through the window formed or, if this proves unsatisfactory, the film will be removed and studied.

The infrared technique will be used for two purposes. The first will be to confirm the presence of any amorphous materials which would not be indicated in the X-ray studies. In addition, if all the materials have characteristic absorption peaks, a quantitative analysis will be attempted.

In the spectrographic studies, projecting the beam through the oxide window or removing the film for a KBr pellet should prove adequate. If sufficient information can be obtained from the infrared and ultraviolet analysis, use of a reflectance attachment will be considered in order to eliminate the chlorine etch step.

The infrared spectrum of silicon dioxide is well known(25), with strong absorption bands in the 9.1 and 12.4 micron regions. The spectra for TiO_2 and Ta_2O_5 are to be determined. This will be accomplished by pressing samples of TiO_2 or Ta_2O_5 in a KBr pellet. Comparison of the spectrum will be made with X-ray results on standard samples.

If a suitable infrared spectrum of all the components in the film can be obtained, a quantitative analysis will be attempted. The basic relationship to be used is Beer's law.

$$I = I_0 \exp(-abc) \quad (10)$$

where: I = Intensity of transmitted radiation
 I_0 = Intensity of the incident radiation
 a = the absorptivity
 b = path length of sample, cm.
 c = concentration of the sample

Equation (10) is applied to a particular absorption peak of wavelength λ . Other useful relations are:

$$T = I/I_0 = \text{transmittance} \quad (11)$$

$$\log I/T = \text{absorbance} = abc$$

Applying equation (10) to a particular material, the value of I_0 will be determined using the base-line technique. This consists of drawing a tangent to each side of the curve around the absorption peak λ .

A vertical line is then drawn through the point of maximum absorption. The intersection of this line with the smoothed tangent curves gives I_0 . This technique consists essentially of drawing a curve as if the absorption peak were not present.

The peak to be chosen for the absorption measurement should show an absorbance of 0.3 to 0.6 for maximum sensitivity. For bands in this absorbance range with a base-line which can be accurately determined, an analytical precision of the order of ± 3 percent of the amount present can be determined.

In order to evaluate c , the concentration of the species whose absorption peak is λ , it is necessary to know a and b in Beer's law. Since b can be considered the distance traveled by the radiation through the oxide film, it can be obtained from a thickness measurement or a weight gain determination using an estimated value of the density. In order to determine a , the absorptivity, it is proposed to oxidize wafers of pure silicon, tantalum and titanium. Since the value of c for these samples would be 100 percent, the value of absorptivity could be determined.

To further characterize the oxide film and its kinetics of growth, thickness measurements will be made. Comparison of the weight gain data for silicides indicates that film thicknesses of the order of 0.5 to 5 microns will be obtained.

A standard optical technique used for measuring the SiO_2 film grown on silicon known as VAMFO(12) (Variable Angle Monochromatic Fringe Observation) is being considered. The apparatus has already been built. The method requires that the film be homogeneous, transparent to visible light and have a reflecting substrate. Preliminary studies indicate that wafers of TiSi_2 and 50 $\text{TiSi}_2 \cdot 50 \text{TaSi}_2$ oxidized at 1400°F (760°C) and 1900°F (1038°C) show interference colors, indicating they are transparent. Homogeneity of the film and a reflecting substrate are still to be established.

In the VAMFO technique, monochromatic light is projected on the sample. The sample is slowly rotated on the stage of a stereomicroscope of approximately 20x. The incident light is partially reflected from the surface of the film and partially transmitted into the film. The transmitted light is reflected from the substrate surface and combines with the partially reflected light at the air-sample surface. When the angle of incidence is such that the two waves interfere destructively, a darkening of the field occurs. Depending on sample thickness, continued rotation gives alternately dark and light areas.

The basic equation used for determining thickness is:

$$d = \lambda \Delta N / 2\mu (\cos r_2 - \cos r_1) \quad (13)$$

where: d = film thickness

λ = wavelength of filtered light

μ = refractive index of film,

ΔN = number of fringes between i_1 and i_2 , where i_j = angle of incidence

r_j = angle of refraction at that fringe for which angle of incidence is i_j and $\sin r_j = (\sin i_j) / \mu$

In order to use this relationship, the refractive index (μ) of the film must be known. A simple method for obtaining this is to immerse the sample in a liquid of refractive index identical to that of the film. When this is done, the film, which in air exhibits interference colors, appears to disappear. Standard solutions(16) of suitable refractive index are available for accomplishing this. The approximate refractive indices of the anticipated oxides that will form are given in Table 1, along with other physical data of interest. If the VAMFO technique proves applicable, additional refinements can be made to improve the accuracy of the results. If not, consideration will be given to other optical techniques such as ellipsometry where, for instance, a sharp reflecting substrate is not critical(13,17).

Expected Results

The initial system being studied is pure TiSi_2 . While Samsonov attributed the protectiveness of this material to the formation of "titanium silicates," the studies described earlier with titanium disilicide additives indicate that TiO_2 (rutile) and SiO_2 (amorphous or cristobalite) are the major products. The phase diagram for this binary system, shown in Figure 6, indicates that no intermediate compounds are formed and that the eutectic melting point is 2822°F (1550°C). Other possible oxides of titanium that are indicated in the literature are Ti_2O_3 , Ti_3O_5 ($\text{Ti}_2\text{O}_3 \cdot \text{TiO}_2$) and TiO (18). SiO_2 is the only stable oxide of silicon that is expected at the conditions proposed for this study, although the form of the SiO_2 whether pure or as a silicate with TiO_2 is to be determined.

Since pure silicon dioxide forms what is probably the best barrier to diffusion of the oxides under consideration, the addition of silicon to the titanium disilicides should improve its oxidation resistance. This will be determined by the relative change in the diffusion coefficient as silicon is added.

Pure TaSi_2 on oxidation forms a non-protective scale consisting of Ta_2O_5 and SiO_2 . Suboxides of tantalum have been reported in the literature(11) for tantalum oxidation, and, as such, their presence will be determined. As silicon is added to TaSi_2 , the oxidation resistance should improve. Silicon will be continually added to pure TaSi_2 until it is not possible to prepare a suitable wafer of sufficient density. If possible, the amount of silicon required to make a wafer of good oxidation resistance will be determined.

Another approach to improving the oxidation resistance of TaSi_2 is to add TiSi_2 . Concentrations of TiSi_2 in TaSi_2 from 0 to 100 percent will be made. The region of protection will be determined. Based on the coating studies, the oxide film should contain Ta_2O_5 , TiO_2 and SiO_2 . The diffusion coefficient in the glass is expected to decrease as more

TiSi₂ is added, but probably not to the same extent as with a comparable amount of silicon. The possible presence of silicates in the protective coating will also be investigated.

The determination of diffusion coefficients and rate constants from experimental data will be carried out using the approach of Deal and Grove(28). With this analysis, the relative importance of the diffusion coefficient and the reaction rate can be determined for all the systems as a function of the temperature, pressure and composition of the substrate.

The Nature of the Diffusing Species

A relatively simple experiment described by Pliskin and Gnall(29) will be carried out to try to determine the nature of the diffusing species. A wafer of titanium disilicide will be oxidized to form an oxide film of about 0.5 microns thickness. The sample will be etched in "P etch" (15HF.10HNO₃.300H₂O) and the film thickness or weight recorded. This will be repeated several times to determine the etch rate of the film. After the etch rate has been determined, the sample will be exposed to phosphorous gas. The sample will then be reoxidized and the etch rate determined. If the etch rate is the same as the earlier determined value, the new oxide was formed on top of the phosphorous marked film indicating silicon and/or titanium is diffusing. If the etch rate is different indicating the phosphorous layer is on top, the oxygen is then the diffusing species.

Progress

A number of wafers of TiSi₂ have been prepared using TiSi₂ powder of 99.8% minimum purity obtained from CERAC. These wafers had densities in excess of 95% of theory and were essentially free of holes. Upon grinding and polishing, a surface with a mirror-like finish was obtained. One of the sintered wafers was powdered and analyzed using X-ray

diffraction. It was found to be identical to the TiSi_2 powder before fabrication indicating a minimum of undesirable reactions occurring during sintering.

Three of the polished wafers were oxidized in air at 1500, 1900 and 2400°F. The sample at 1500° showed a weight gain of only 0.1 mg/cm² after 67 hours of oxidation. This is equivalent to that obtained on oxidation of pure silicon which is known to form an extremely impervious SiO_2 film. At 1900°F a weight gain of 0.4 mg/cm² was obtained after 84 hours, while at 2400°F a weight gain of 1.4 mg/cm² was obtained after 96 hours. Little weight change was observed in any of the specimens after the initial 40 hours. The samples at 1500 and 1900°F had films which exhibited interference colors similar to those obtained when pure silicon is oxidized. At 2400°F the oxide film appeared glassy and non-uniform with no interference colors.

The oxide film formed on the sample at 1900°F was analyzed using X-ray diffraction and infrared spectroscopy. In order to isolate the film, a ¼" diameter hole was drilled in the back of the specimen to a depth of 2/3 of the way through the wafer. The sample was then placed in chlorine at 900°C for 10 minutes to remove the remaining silicide in the hole. An oxide window was thus obtained. When this was placed in the path of the infrared beam no transmission was obtained. Part of the film was then removed, mixed with KBr and pressed into a clear pellet. When this was examined in the infrared spectrophotometer, absorption peaks characteristic of silicon-oxygen vibrations were clearly observed.

The remainder of the oxide window was removed and powdered for X-ray analysis. The resulting powder pattern indicated TiO_2 (rutile) as the only material present. No SiO_2 lines were observed. This would appear to indicate that the SiO_2 is present in an amorphous form either pure or as a silicate. Further study will be carried out on new infrared equipment, soon to be delivered. This equipment is capable of analyzing

beyond 15 microns where Ti-O vibrations should be found.

Two additional wafers of 60 weight % TaSi₂, 40 weight % TiSi₂ were prepared. Upon sintering a density of about 90% of theoretical was obtained. However, the surface contained a number of small holes. Oxidation for 44 hours at 1900°F produced a weight gain of 1.0 mg/cm²; at 2400°F for 44 hours a gain of 1.5 mg/cm². The 1900°F specimen exhibited interference colors similar to that for pure TiSi₂ at 1900°F. The film on the 2400°F sample was rough and uniform but not glassy as was the film on pure TiSi₂ at 2400°F. Analysis of this film is in progress.

Oxidation Rates and Coating Modifiers

The work described in the previous section was concerned with providing fundamental understanding of glasses formed in silicide oxidation by analyzing the protective and non-protective glasses. At the same time, it is possible to attempt synthesis of protective glasses on the basis of existing principles for glass formation. The technique of manufacturing wafers by powder metallurgy methods lends itself readily to the introduction of modifiers. The composite material may then be evaluated by oxidation rate studies to determine the degree of success.

The likely effects of various cations upon the stability of a silica glass may be estimated from their ionic radii and valence in terms of ionic field strength(66) or in terms of single bond strengths(67). The rules that have been proposed for stability of glasses are described by Kingery(68). Using these principles, modifiers will be selected, included in wafers and tested for their effects on oxidation resistance.

Empirically, it is known that modifiers such as vanadium and titanium do minimize pest formation and promote the formation of self-healing glasses(10,51). Additional tests with a variety of elements are described by Regan(60), who obtained marked improvement by the addition of borax. However, no workers have attempted to "design" silicide coatings in terms of fundamental principles.

Although most of the work will be performed with disilicides, trisilicides, although nonprotective at normally protective temperatures for disilicides, are also of interest since they otherwise possess some desirable attributes. As a consequence of their inherently lower silicon activity, the tendency to dissociate to lower silicides markedly lessened. If used as a coating on pure metal substrates (M_5Si_3 on M) trisilicides will also be more stable to silicon loss by diffusion to the substrate.

Since eutectic temperatures for these intermediate silicides are

higher than corresponding disilicides they will have a higher service temperature capability. For example, $Ta_{4.5}Si - Ta_2Si$ melts at $2400^{\circ}C$ while $Ta_5Si_3 - TaSi_2$ melts at $2100^{\circ}C$. The chief disadvantage of trisilicides is their initially higher oxidation rate (longer times required to form protective glazes) and the relatively high active-to-passive transition temperature which must be either eliminated or lowered if they are to be useful.

Experimental Method

Specimens will be fabricated in the form of disks by powder metallurgy techniques. By this method, modifiers can be added with little difficulty. The specimens will be oxidized at temperatures up to $2500^{\circ}F$ and oxygen pressures up to one atmosphere. The rate of oxidation will be determined by weighing, and a comparison of the rates will form the basis for comparison of the selected modifiers. The specimens will be sectioned for microscopic examination along with microhardness traverses (to detect interstitial embrittlement). If protective glasses form, X-ray and chemical analysis will establish whether they are complex silicates, duplex or higher mixed oxides, or simply some form of pure SiO_2 (silica) such as α -cristobalite.

The work to date has been primarily concerned with equipment procurement and construction, development of specimen fabrication techniques, grinding and polishing.

Straight silicides of better than 90% theoretical X-ray density have been fabricated with reproducibility in this laboratory by the following procedure:

- (1) Synthesis of silicides from base metal and silicon (in slight excess to accommodate evaporative losses).
- (2) Grinding and screening to a fine mesh size ($-325 + 400$ or finer).
- (3) Addition of 0.5-1% sintering aide (usually Ni).

(4) Cold Press at 5-10 tons per square inch using less than 1-2% binder such as poly-methylmethacrylate.

(5) Pre-sintering in vacuo to drive off binder (below red heat).

(6) Sintering in vacuo.

(7) Grinding with diamond grinding discs and polishing with diamond pastes followed by gamma alumina final polish. A complete grinding and polishing scheme has been evolved and tested. Two-step fine grinding is accomplished with resin bonded diamond grinding discs and water as a lubricant. Rough polishing is performed on nylon using 6 μ diamond paste with a lapping oil. Fine polishing in a similar fashion using 3 μ diamond paste, and a final polish (only 1-2 min.) using 0.05 gamma alumina on Texmet with water as the lubricant gives a highly satisfactory surface.

(8) Solvent wash followed by drying over activated alumina or silica gel. Specimen wafers so prepared weigh about a gram and are approximately 1/2" in diameter by 1/32" thick.

Modified silicides can be prepared using additives in elemental form or as silicides.

Oxidation furnaces employing globar heating elements are being built. A prototype model has been built and found satisfactory. Static air tests are presently performed with a variety of box furnaces on hand (maximum capability of 2500 $^{\circ}$ F).

The selection of specimen support material is critical, since severe attack by alumina and mullite and slight attack by fused quartz have been noted by previous investigators. Fused quartz hooks made for use in the model furnace have seemed adequate. Small holes are drilled in the specimen wafers with a diamond tip drill bit. Thus specimens can be suspended vertically in the furnace.

Some preliminary oxidation tests have been made on TaSi₂ in static air at approximately 2500 $^{\circ}$ F. The weight gains were appreciably greater than those reported for MoSi₂ under similar conditions. A pale yellow coating (probably Ta₂O₅) was observed to uniformly cover the surface of the exposed TaSi₂ specimens.

Substrate-Coating Interaction and Barriers

The service lifetimes of disilicide coatings are shortened because they interact by diffusion with the metallic substrates to form lower silicides, such as Ta_5Si_3 . The latter are unable to form the protective glassy oxide, presumably because of the simultaneous formation of the substrate metal oxide. Therefore, an understanding of the mechanism of growth of the lower silicide layer and its inhibition is an important approach to increasing the coating life.

The growth kinetics of Ta_5Si_3 in the Ta/ $TaSi_2$ system and of Cb_5Si_3 in the Cb/ $CbSi_2$ system will be investigated in an effort to inhibit the growth of the lower silicides. The rate of growth of a trisilicide such as Ta_5Si_3 is controlled by its permeability to Ta and Si, and it is this diffusion process which will first be studied. The individual fluxes of Ta and Si will be measured using diffusion anneal couples of Ta wafers and $TaSi_2$ wafers. Subsequent work will include columbium.

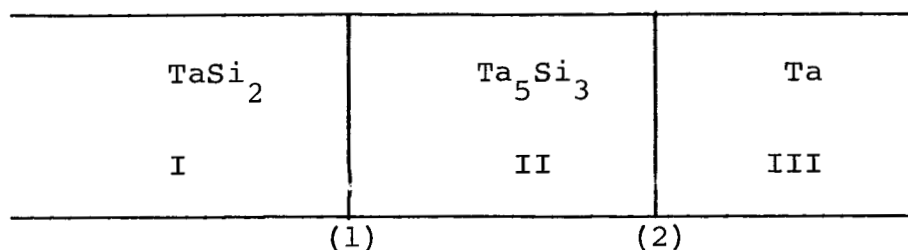
The general approach will consist of bringing wafers of the substrate metal and coating material into contact under pressure at the elevated temperatures of interest. The rates of growth of the intermediate silicides will be measured. At the same time, marker experiments will be performed to determine the relative rates of diffusion of metal and silicon. The same techniques will then be applied to measure and explain the performance of additive or barrier elements such as titanium and chromium.

Theory

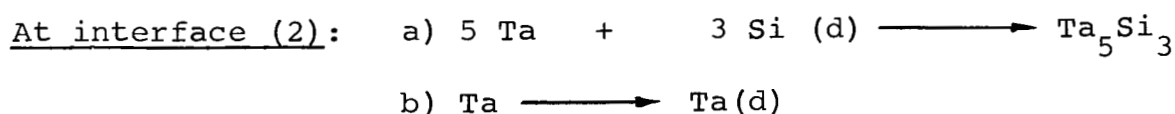
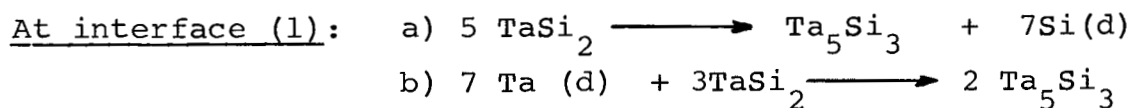
From consideration of the Ta/Si phase diagram (Fig.3) the interdiffusion of Ta and $TaSi_2$ produces three intermediate silicides.

$TaSi_2$	Ta_5Si_3	Ta_2Si	$Ta_{4.5}Si$	Ta
I	II	III	IV	V
(1)	(2)	(3)	(4)	

Experiments, however, show that as long as the disilicide is present, only trisilicide forms in appreciable amounts(10). Thus the two lower silicides are neglected in the following derivation. A more detailed analysis including Ta_2Si and $Ta_{4.5}Si$ with negligible growth rates yields the same results.



In the simplified system above, I, II and III indicate the phases and (1) and (2) indicate interfaces. First the reactions at each interface are written. From steric considerations it may be argued that reactions occur only at interfaces. Si(d) indicates silicon diffusing from interface (1) to interface (2) through phase II. Similarly Ta(d) indicates tantalum diffusing from interface (2) to interface (1) through phase II.



During the growth of the intermediate phase the reactions are diffusion controlled, and the growth rate of any compound is dependent upon the fluxes J of the diffusing components across the phase boundaries. Therefore, the rate of formation r of Ta_5Si_3 in moles per unit time per unit cross-section area is:

$$r_1 = 1/7 J_{Si} - 2/7 J_{Ta}$$

at interface (1), and

$$r_2 = 1/3 J_{Si}$$

at interface (2).

The total rate of formation of Ta_5Si_3 is the sum of the rates at interface (1) and interface (2).

$$r = 10/21 J_{Si} - 2/7 J_{Ta} \quad (14)$$

If Fick's law is applied, the various species fluxes can be expressed in terms of concentration gradients.

$$J_i = -D_i \frac{dC_i}{dx} \quad (15)$$

In a multiphase system there is one such equation for each phase. Since the growth of Ta_5Si_3 is controlled only by the diffusion through Ta_5Si_3 (phase II) Fick's Law for this system may be written as:

$$J_{iII} = -D_{iII} \frac{dC_{iII}}{dx_{II}} \quad (16)$$

where $i = Ta$ or Si .

Applying this expression to equation (1), the rate equation becomes:

$$r = -\frac{10}{21} \left[D_{SiII} \frac{dC_{SiII}}{dx_{II}} \right] + \frac{2}{7} \left[D_{TaII} \frac{dC_{TaII}}{dx_{II}} \right] \quad (17)$$

Since the whole equation involves only phase II (Ta_5Si_3), the subscript (II) may be dropped for simplicity. The concentration change across the phase is small because the phase is nearly stoichiometric. Therefore, the diffusion coefficients, D_{Si} and D_{Ta} , are assumed constant across the phase. At steady state, in consequence, the concentration gradients are constant.

$$\frac{dC_{Si}}{dx} = -\frac{\Delta C_{Si}}{\Delta X} \quad \text{and} \quad \frac{dC_{Ta}}{dx} = \frac{\Delta C_{Ta}}{\Delta X}$$

where ΔC_{Si} and ΔC_{Ta} are the small concentration changes across phase II and ΔX is the thickness of that phase.

Using this in eq. (4)

$$r = \left[10/21 D_{Si} \Delta C_{Si} + 2/7 D_{Ta} \Delta C_{Ta} \right] 1/\Delta X \quad (18)$$

If equilibrium is assumed at the interfaces, the ΔC 's are constant for all values of ΔX . The term in brackets, therefore, may be regarded as the product of an average diffusivity, \bar{D} , with an appropriate ΔC .

$$r = \bar{D} \Delta C (1/\Delta X) \quad (19)$$

The rate of growth can be expressed as a change in thickness as long as the molar density is constant.

$$r = \left(\rho/M \right) \frac{d(\Delta X)}{dt} = \bar{D} \Delta C (1/\Delta X) \quad (20)$$

where M and ρ = molecular weight and density of Ta_5Si_3 respectively.

On integration of eq. (20) the parabolic rate expression is obtained.

$$(\Delta X)^2 = 2 \frac{(M)}{\rho} \bar{D} \Delta C t \quad (21)$$

The concentration changes, ΔC_{Si} and ΔC_{Ta} , have not been accurately measured and therefore ΔC is not known. But ΔC should be a constant for the system, depending only on the thermodynamic solubility of the species. \bar{D} and ΔC will be combined and called \underline{D} . This quantity is not basically a diffusion coefficient (the units of \underline{D} are moles / sec-cm). Although it lacks fundamental significance, \underline{D} is a

variable which accurately describes the growth rate of the intermediate phase. The working equation in what follows is therefore

$$(\Delta X)^2 = 2 \frac{(M)}{\rho} \underline{D} t \quad (22)$$

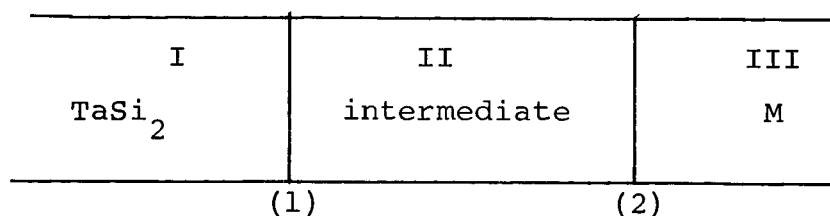
Equation (22) will be used in calculating \underline{D} from the change in thickness of the trisilicide layer. Since the concentration distribution of the diffusing species is constant in the Ta_5Si_3 layer, \underline{D} will be a function of temperature only, and a set of ΔX vs. t data will apply to a specific temperature. \underline{D} may be correlated with

temperature by the usual Arrhenius expression

$$\underline{D}(t) = \underline{D}_0 e^{-Q/RT} \quad (23)$$

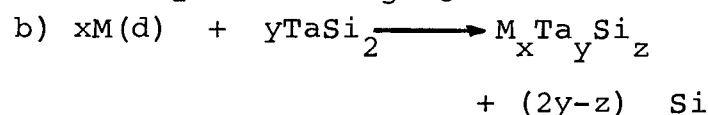
Additives and Barriers

The effects of additives on the growth of the intermediate phase will be tested by coupling TaSi_2 (and later Cb Si_2) with selected refractory metals other than Ta. Metals that form intermediate phases slowly may be considered good barrier materials if the diffusional degradation of TaSi_2 is sufficiently retarded. A working equation for the M/TaSi_2 system can be derived using the approach employed above for the Ta/TaSi_2 system.



First the possible interfacial reactions are written.

At interface (1): a) $5\text{TaSi}_2 \longrightarrow \text{Ta}_5\text{Si}_3 + 7 \text{ Si (d)}$



At interface (2): a) $x\text{M} + z \text{ Si(d)} \longrightarrow \text{M}_x\text{Si}_z$

b) $\text{M} \longrightarrow \text{M(d)}$

Phase II will therefore consist of Ta_5Si_3 , M_xSi_z (metal silicide) and possibly $\text{M}_x\text{Ta}_y\text{Si}_z$ (mixed silicide).

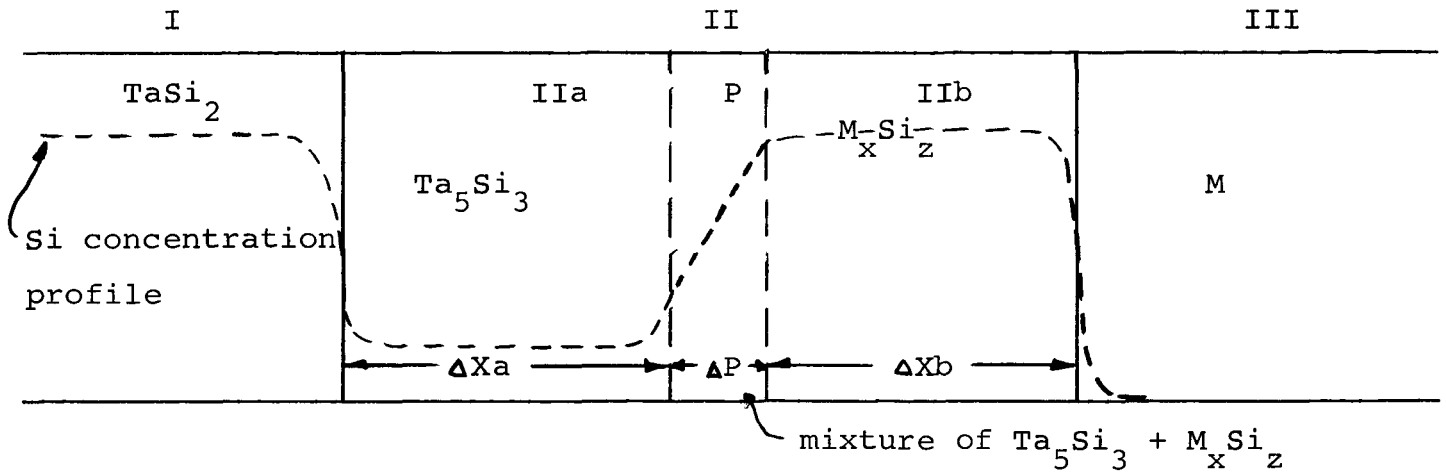
The rates of growth of these intermediates can be expressed in terms of the fluxes of the diffusing species.

At interface (1): a) $r(\text{Ta}_5\text{Si}_3) = 1/7 J_{\text{Si}}$

b) $r(\text{M}_x\text{Ta}_y\text{Si}_z) = 1/x J_{\text{M}}$

At interface (2): a) $r (M_x Si_z) = 1/z J_{Si}$

If the formation of the mixed silicide is unfavorable thermodynamically or if M diffusion is negligible compared to Si diffusion the system is considerably simplified. The latter assumption can be checked by marker experiments, whereas the former assumption can not be checked because of the lack of thermodynamic data. Assuming negligible $M_x Ta_y Si_z$ formation, the diffused couple would look as follows:



The rate of growth of intermediate phase II is

$$r_{II} = r (Ta_5Si_3) + r (M_x Si_z) \quad (24)$$

$$\text{or } r_{II} = \frac{z + 7}{7z} J_{Si}$$

$$\text{with } J_{Si} = -D_{Si_{II}}(c) \frac{dc_{Si_{II}}(x)}{dx_{II}} \quad (25)$$

where $D_{Si_{II}}(c)$ can be considered constant but different in regions IIa and IIb, and a function of x in region P.

If the P phase is assumed to be very small, its presence may be neglected and the derivation simplified.

Across the interface between IIa and IIb the concentrations of Si are connected by an equilibrium relation. ΔX_a and ΔX_b are in the

fixed ratio 7/z by stoichiometry. With the constancy of C_{Si} at the ends of region II, it follows that $(\Delta C_{Si})_{IIa}$ and $(\Delta C_{Si})_{IIb}$ are fixed for all thicknesses. Therefore

$$J_{Si} = D_{IIa} \frac{(\Delta C_{Si})_{IIa}}{\Delta X_a} = D_{IIb} \frac{(\Delta C_{Si})_{IIb}}{\Delta X_b} \quad (26)$$

By defining \underline{D}_{Si} as

$$\underline{D}_{Si} = D_{IIa} (\Delta C_{Si})_{IIa} \frac{\Delta X_a}{\Delta X_{II}} = D_{IIb} (\Delta C_{Si})_{IIb} \frac{\Delta X_b}{\Delta X_{II}}$$

equation (26) becomes

$$J_{Si} = \underline{D}_{Si} \frac{1}{X_{II}} \quad (27)$$

This value for J_{Si} is now put into the expression for the phase II rate of growth.

$$r_{II} = \frac{z+7}{7z} \left[\underline{D}_{Si} \frac{1}{\Delta X_{II}} \right] \quad (28)$$

Since $D_M = 0$ in this derivation,

$$r_{II} = \underline{D}_{II} \left(\frac{1}{\Delta X_{II}} \right) \quad (29)$$

The working equation now becomes

$$(\Delta X_{II})^2 = 2 \left(\frac{M}{\rho} \right)_{IIav} \underline{D}_{II} t \quad (30)$$

Where $\left(\frac{M}{\rho} \right)_{IIav}$ = mole fraction $(Ta_5Si_3) \left(\frac{M}{\rho} \right)_{Ta_5Si_3} + \text{m.f. } (M_xSi_z) \left(\frac{M}{\rho} \right)_{M_xSi_z}$

$$\text{which} = \frac{\Delta X_{II}}{\Delta X_a \left(\frac{\rho}{M} \right)_{Ta_5Si_3} + \Delta X_b \left(\frac{\rho}{M} \right)_{M_xSi_z}}$$

\underline{D}_{II} is equivalent to the \underline{D} defined earlier, since it describes the growth rate of the intermediate phase. For convenience, \underline{D} or \underline{D}_{II} can be called a rate coefficient or growth rate coefficient or growth coefficient, so as not to be confused with an actual diffusion coefficient, D , or an average diffusivity, \bar{D} .

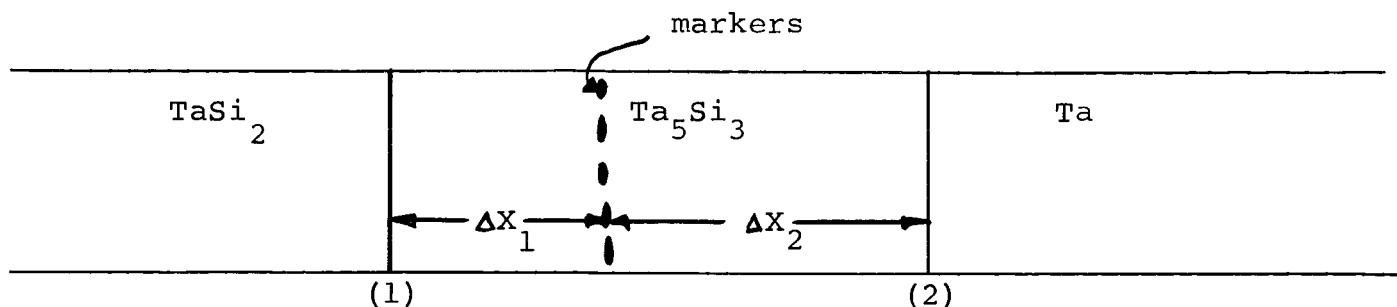
If the formation of the mixed silicide cannot be neglected, a new rate coefficient must be defined including D_{Ta} and ΔC_{Ta} as extra terms.

Markers

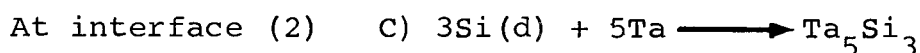
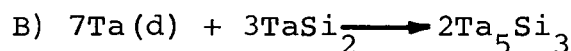
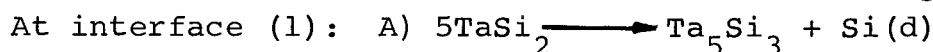
Markers will be employed to determine the magnitudes of the individual growth rate coefficients in the Ta/TaSi₂ and Cb/CbSi₂ systems and will provide an understanding of the mechanism of diffusion. The marker technique has been used frequently in oxidation studies, where the marker is attached to a clean metal surface and the metal then oxidized. If the oxygen is the only diffusing species, the marker will remain at the gas-solid interface. If the metal is the diffusing species, the marker will become embedded in the oxide at the solid-solid interface.

In the Ta/TaSi₂ or Cb/CbSi₂ system, as the intermediate grows, a marker at the original interface will indicate the relative fluxes of the diffusing species, such as Ta and Si. In this case, the relationship is not as simple as in the oxidation experiments because the trisilicide is formed both by the departure of silicon from the disilicide (equation A below), the reaction of silicon with tantalum (equation C) and the reaction of tantalum with the disilicide (equation B).

From stoichiometry the ratio between the distance of the marker from the Ta/Ta₅Si₃ interface, ΔX_2 , and the distance of the marker from the TaSi₂/Ta₅Si₃ interface, ΔX_1 , can be derived.



The reactions at each interface that produce Ta_5Si_3 are:



Using the same argument as was used to derive a working growth rate expression in the previous section, relations indicating the growth rate of Ta_5Si_3 to the left of the marker (or original interface) and the growth rate of Ta_5Si_3 to the right of the marker can be independently derived.

The rate to the left of the markers is the rate due to reactions occurring at interface (1) (equations A and B), and the growth to the right of the markers is due to reactions at interface (2) (equation C).

$$\text{rate (1)} = 1/7 J_{Si} - 2/7 J_{Ta} \quad (31)$$

$$\text{rate (2)} = 1/3 J_{Si} \quad (32)$$

Applying Fick's law and the relations

$$\text{rate (1)} = \frac{(\rho)}{M} \frac{d(\Delta X_1)}{dt} \quad \text{and} \quad \text{rate (2)} = \frac{(\rho)}{M} \frac{d(\Delta X_2)}{dt}$$

two differential equations result.

$$\frac{(\rho)}{M} \frac{d(\Delta X_1)}{dt} = -1/7 D_{Si} \frac{dC_{Si}}{dX_1} + 2/7 D_{Ta} \frac{dC_{Ta}}{dX_1} \quad (33)$$

$$\left(\frac{p}{M}\right) \frac{d(\Delta X_2)}{dt} = -1/3 D_{Si} \frac{dC_{Si}}{dX_2} \quad (34)$$

using

$$\frac{dC_{Si}}{dX} = \frac{-\Delta C_{Si}}{\Delta X}$$

and integrating, parabolic relations for (ΔX_1) and (ΔX_2) result.

$$(\Delta X_1)^2 = 2 \left(\frac{M}{p}\right) (1/7 D_{Si} \Delta C_{Si} + 2/7 D_{Ta} \Delta C_{Ta}) t \quad (35)$$

$$(\Delta X_2)^2 = 2/3 \left(\frac{M}{p}\right) (D_{Si} \Delta C_{Si}) t \quad (36)$$

Dividing equation (36) by equation (35), a ratio between (ΔX_2) and (ΔX_1) results.

$$\frac{(\Delta X_2)^2}{(\Delta X_1)^2} = \frac{2/3 D_{Si} \Delta C_{Si}}{2/7 D_{Si} \Delta C_{Si} + 4/7 D_{Ta} \Delta C_{Ta}} \quad (37)$$

Calling $\underline{D}_i = D_i \Delta C_i$ and simplifying yields the final form of the working equation which will define the magnitudes of the individual rate coefficients.

$$\frac{(\Delta X_2)^2}{(\Delta X_1)^2} = \frac{7 \underline{D}_{Si}}{3 \underline{D}_{Si} + 6 \underline{D}_{Ta}} \quad (38)$$

From the above relationship it can be seen that although the marker will be at the Ta/Ta₅Si₃ interface when Ta is the only diffusing species ($\underline{D}_{Si} = 0$), the marker will not be at the TaSi₂/Ta₅Si₃ interface when Si alone diffuses ($\underline{D}_{Ta} = 0$); but rather at a spot between the two interfaces such that $\frac{(\Delta X_2)^2}{(\Delta X_1)^2} = 7/3$. Therefore, the ratio of the

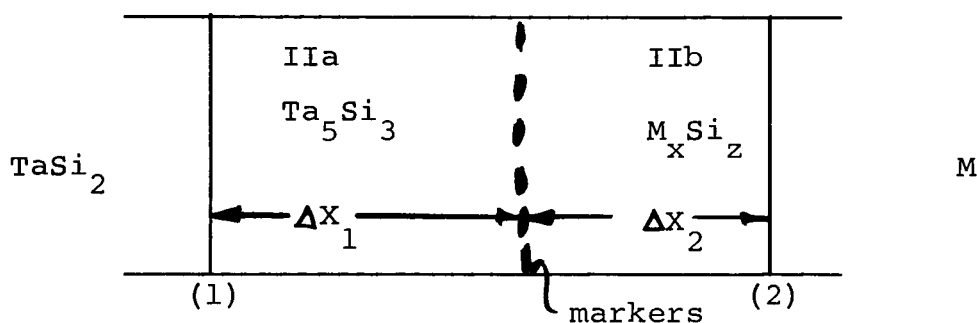
individual rate coefficients can be calculated by noting the position of the markers. Since $\underline{D} = 10/21 \underline{D}_{Si} + 2/7 \underline{D}_{Ta}$, from the definition of

\underline{D} , \underline{D}_{Si} and \underline{D}_{Ta} can be found. Alternately, \underline{D}_{Si} and \underline{D}_{Ta} can be found directly from equations (22) and (23) and \underline{D} computed from the definition above.

The main purpose of the marker in the $M/TaSi_2$ is to determine if Si is the only diffusing species to be considered. If $\underline{D}_M = 0$, the equations for intermediate formation can be written in a simplified form.

At interface (1): A) $5TaSi_2 \longrightarrow Ta_5Si_3 + 7Si(d)$

At interface (2): B) $xM + zSi(d) \longrightarrow M_xSi_z$



$$\text{rate (1)} = 1/7 J_{Si} \quad (39)$$

$$\text{rate (2)} = 1/z J_{Si} \quad (40)$$

Again a parabolic rate results.

$$(\Delta X_1)^2 = 2/7 \left(\frac{M}{\rho} \right) Ta_5Si_3 \underline{D}_{Si} t \quad (41)$$

$$(\Delta X_2)^2 = 2/z \left(\frac{M}{\rho} \right) M_xSi_z \underline{D}_{Si} t \quad (42)$$

Therefore, if $\underline{D}_M = 0$, the critical ratio should be:

$$\frac{(\Delta X_2)^2}{(\Delta X_1)^2} = \frac{z}{7} \frac{(M/\rho) M_xSi_z}{(M/\rho) Ta_5Si_3} \quad (43)$$

If the mixed phase, P, grows in discernible amounts between the Ta_5Si_3 and M_xSi_z layers, marker placement may be complicated by the

shifting of atomic planes known as the Kirkendall effect(57). This effect is observed in binary alloy diffusion in which a net flow of vacancies causes marker motion through the alloy. Darken(58) has developed a method of analysis for this phenomenon as well as for multi-component systems, which will be employed only if necessary. (M/ρ) values will also have to be corrected, taking into account the relative amounts of Ta_5Si_3 and M_xSi_z in the mixed phase.

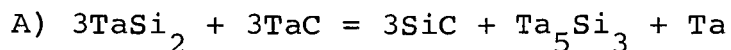
If the mixed silicide $(M_xTa_ySi_z)$ is formed, the ratio of \underline{D}_M to \underline{D}_{Si} can be calculated once the composition of this compound is determined.

Selection of Marker Material

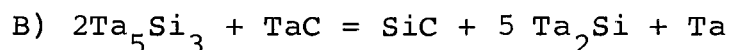
The marker itself should be completely inert to the environment surrounding it. At the temperatures involved one must resort to very stable, high temperature carbides or oxides to avoid reaction or vaporization.

Thermodynamic properties may be employed to help select stable marker materials. Free energies for reaction with Ta, $TaSi_2$ and Ta_5Si_3 were used to determine the probability of reaction. Free energy data for the carbides and oxides were taken from Bureau of Mines Bulletin 605(59). Data for the free energies of formation of the silicides were estimated from heat of formation data given by Greivson and Alcock(59) and Robins and Jenkins(30). The data for the silicides are not reliable, but do not affect the major conclusions. Further explanation of data is given in the calculations.

TaC is a natural choice for a marker material because it is one of the most stable carbides and its use reduces side-reactions. The reactions for which free energies were calculated are:



$$\Delta G = + 26 \text{ Kcal/mole TaC}$$

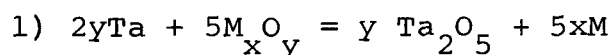


$$\Delta G = + 80 \text{ Kcal/mole TaC}$$

Since temperature dependence was small, the above ΔG 's are an average over the temperature range of interest. The positive values of ΔG indicate that the reactions will not proceed.

TiC was evaluated in a similar manner, and although ΔG was also positive the TaC proved more thermodynamically stable and is the first choice.

Oxide calculations were made and plotted as a function of temperature. The plots are based on the three most probable reactions, ignoring the formation of silicates and other possible side reactions. Reaction 1) takes place with Ta.

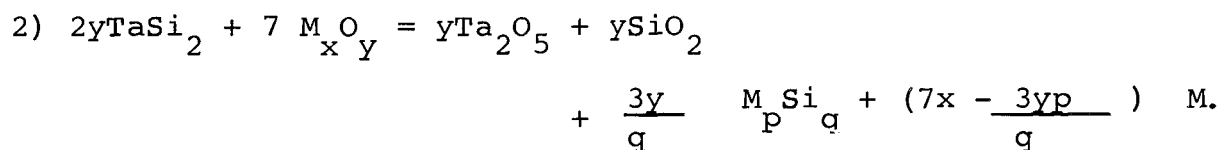


$$\frac{\Delta G}{\text{mole Ta}_2\text{O}_5} = \Delta G_f (\text{Ta}_2\text{O}_5) - \frac{5}{y} \Delta G_f (\text{M}_{\text{x}}\text{O}_{\text{y}})$$

The results of reaction 1) are plotted in Figure 7 as

$\Delta G_f (\text{Ta}_2\text{O}_5)$ (line A) and (B) lines showing $\frac{5}{y} \Delta G_f (\text{M}_{\text{x}}\text{O}_{\text{y}})$ for different oxides. Using this scheme, the (B) line which is most negative would give the largest positive ΔG for the reaction and would be the best choice for a marker material.

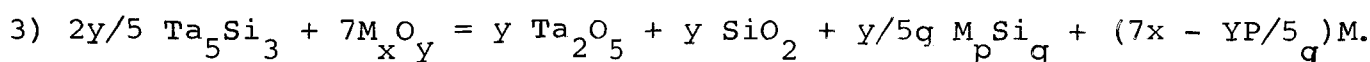
Reaction 2) takes place with TaSi_2 .



$$\frac{\Delta G}{\text{mole Ta}_2\text{O}_5} = \left[\Delta G_f (\text{Ta}_2\text{O}_5) + \Delta G_f (\text{SiO}_2) - 2 \Delta G_f' (\text{TaSi}_2) \right] \quad (\text{A})$$

$$- \left[7/y \Delta G_f (\text{M}_{\text{x}}\text{O}_{\text{y}}) - 3/q \Delta G_f (\text{M}_{\text{p}}\text{Si}_{\text{q}}) \right]. \quad (\text{B})$$

Reaction 3) takes place with Ta_5Si_3 .



$$\frac{\Delta G}{\text{mole Ta}_2\text{O}_5} = \left[\Delta G_f (\text{Ta}_2\text{O}_5) + \Delta G_f (\text{SiO}_2) - \frac{2}{5} \Delta G_f (\text{Ta}_5\text{Si}_3) \right] \quad (\text{A})$$

$$- \left[7/y \Delta G_f (\text{M}_x\text{O}_y) - 1/5q \Delta G_f (\text{M}_p\text{Si}_q) \right]. \quad (\text{B})$$

The results of reactions 2) and 3) are presented in Figure 8. Again the (B) lines that are most negative would be the best choices for marker materials.

In each case, Y_2O_3 and CaO show the best stability and would normally be the first choice as oxide markers.

ThO_2 is a close runner-up and MgO appears to be a possibility. Since yttria and thoria may be reduced to compounds that are sub-stoichiometric in oxygen, the CaO and MgO markers may prove more stable in practice.

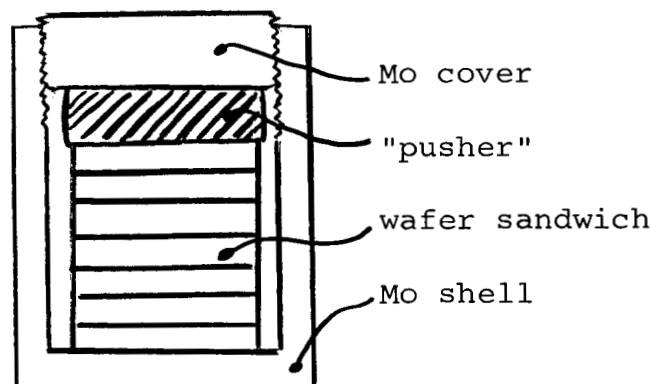
Selection of Additives or Barrier Materials

Materials that have been tested empirically and have shown to improve the oxidation resistance of disilicide coatings, such as Cr and Ti , will be used in the diffusion barrier experiments (61). Theoretically these materials should inhibit the diffusional degradation of the disilicide. Intermediates formed and their structures will be identified by X-ray analysis, and efforts will be made to relate these structures and their properties to the barrier effects observed.

Apparatus

Diffusion anneals will be carried out in a SiC furnace designed for heating in an inert atmosphere. Sample wafers, after polishing and cleaning, will be packed in a sandwich arrangement and sealed in a container designed to apply pressure upon heating because of the difference in thermal expansions between the molybdenum shell and a

"pusher" slug. Use was made of thermal expansions and mechanical property data(62-65) to calculate the container dimensions necessary to produce a pressure of about 1000 psi average. A sketch of the container is given below.



After the anneal, the wafer sandwich will be sectioned, polished and etched, and examined microscopically. Phase thicknesses will be measured and the phases will be identified by X-ray analysis.

An alternative to the thermal expansion approach for the application of pressure during the anneal is a modification of the commonly used creep test apparatus. In this set-up a load could be applied externally and kept at a constant value. The design is more complicated than the container arrangement and will be employed only if there are unexpected difficulties with the simpler system.

Progress

The equipment for the diffusion anneal experiments has been designed, procured and almost completely built. Basically it consists of globar furnaces arranged to receive fused quartz tubes which will contain an argon atmosphere and the specimen "clamp." The argon inlet is in the same line as a quick coupling O-ring seal used to grasp the molybdenum support rod. This support rod will raise and

lower the specimen "clamp" in and out of the heating zone of the furnace so that the heat-up and cool-down periods of the specimens will be negligible compared to the actual diffusion time.

The specimen clamp is made from solid molybdenum stock and is basically a hollow cylinder with threaded ends. The specimen wafers will be loaded into the clamp in a sandwich arrangement, a "pusher" slug inserted and the top screwed down to ensure mechanical contact. As the clamp heats up, the difference in thermal expansions of the Mo body and "pusher" will exert sufficient pressure on the wafers to provide for proper diffusion.

Runs will be made at temperatures between 1500^oF and 2500^oF at 200^oF intervals.

Program for Next Six-Month Period

1. Thermochemical Data: As soon as tests on the improved EMF cell are completed, measurements on the appropriate silicide electrodes will be made. Compositions will be checked by X-ray diffraction. It is expected that several of the desired free energies of formation of the tantalum silicides will be obtained.
2. Glass Structure and Growth: Additional specimens of TiSi_2 are being prepared. These will be oxidized to test the suitability of the VAMFO, x-ray diffraction, and infrared reflectance techniques. Materials for a new oxidation furnace are being procured and this will be built.
3. Oxidation Rates Coating Modifiers: Oxidation rates of bulk TaSi_2 and Ta_5Si_3 will be measured. Specimens containing selected modifiers will be fabricated and oxidation measurements on these samples will be started.
4. Substrate-Coating Interaction and Barriers:
The diffusion-anneal furnace is under construction. The growth of the intermediate phase in the TaSi_2 - Ta system will be measured and marker experiments started.

Table 1
Properties of Oxides

<u>Material</u>	<u>Form</u>	<u>MW</u>	<u>MP</u>	<u>o</u>	<u>F</u>	<u>(o C)</u>	<u>Density, g/cm</u>	<u>Refract Index</u>	<u>Color</u>
Ta_2O_5		441.8	3434			(1890)	8.02	2 ^a	
TiO_2	rutile	79.9	3344			(1840)	4.24	2.6 ^b	white ^d
SiO_2	quartz	60.1	3142			(1728)	2.65	1.5 ^c	
SiO_2	cristobalite	60.1	3142			(1728)	2.32	1.5 ^c	
SiO_2	vitreous	60.1	3142			(1728)	2.20	1.5 ^c	
Ti_2O_3 ^d						(1900-2130 ^d)	4.6 ^d		dark violet ^d
TiO ^d						(1750-2020 ^d)	4.93 ^d		golden yellow ^d

1. All data except refractive indices from Reference 18.

a. Reference 19

b. Reference 20

c. Reference 21

d. Reference 15

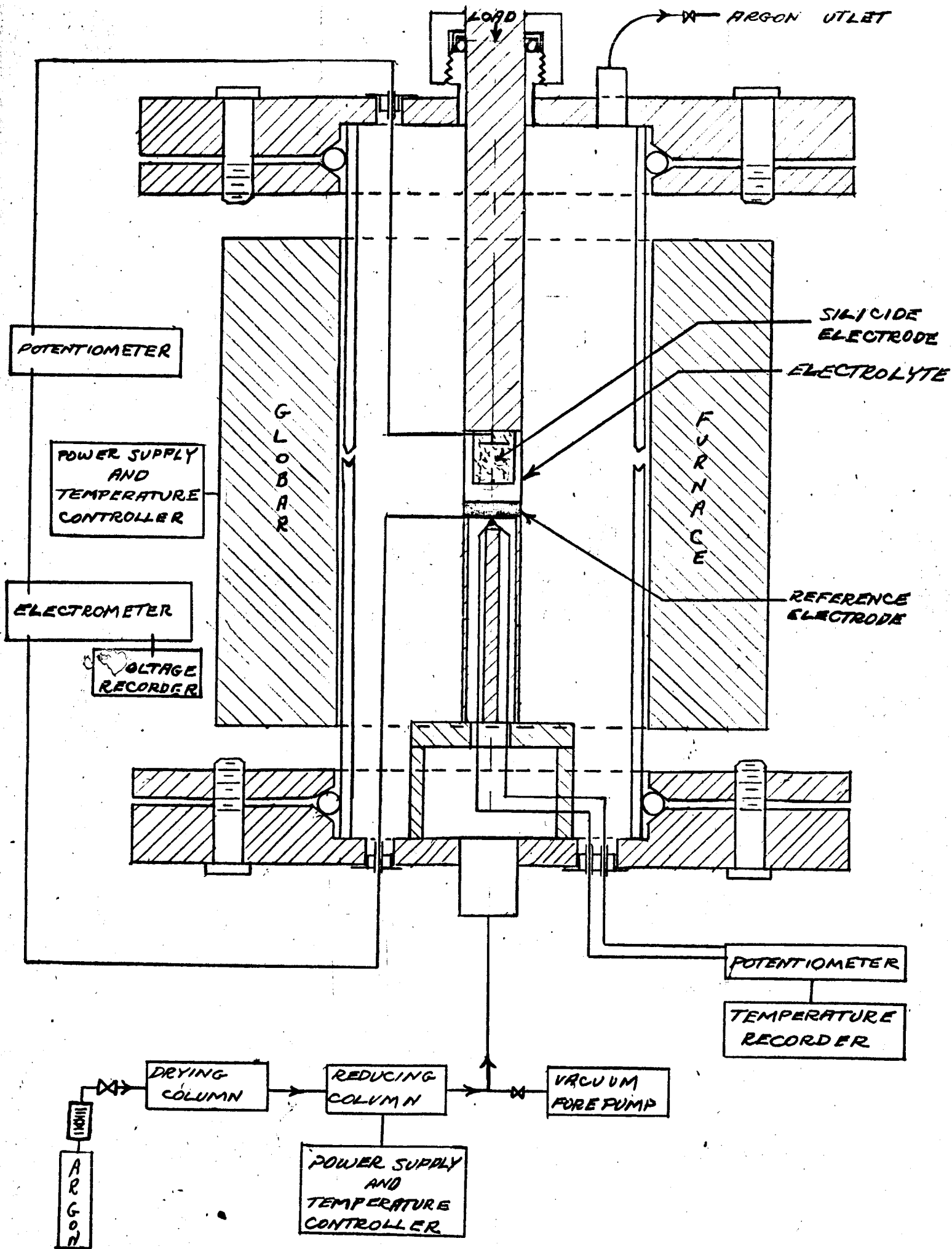


FIGURE 1. APPARATUS FOR EMF MEASUREMENTS

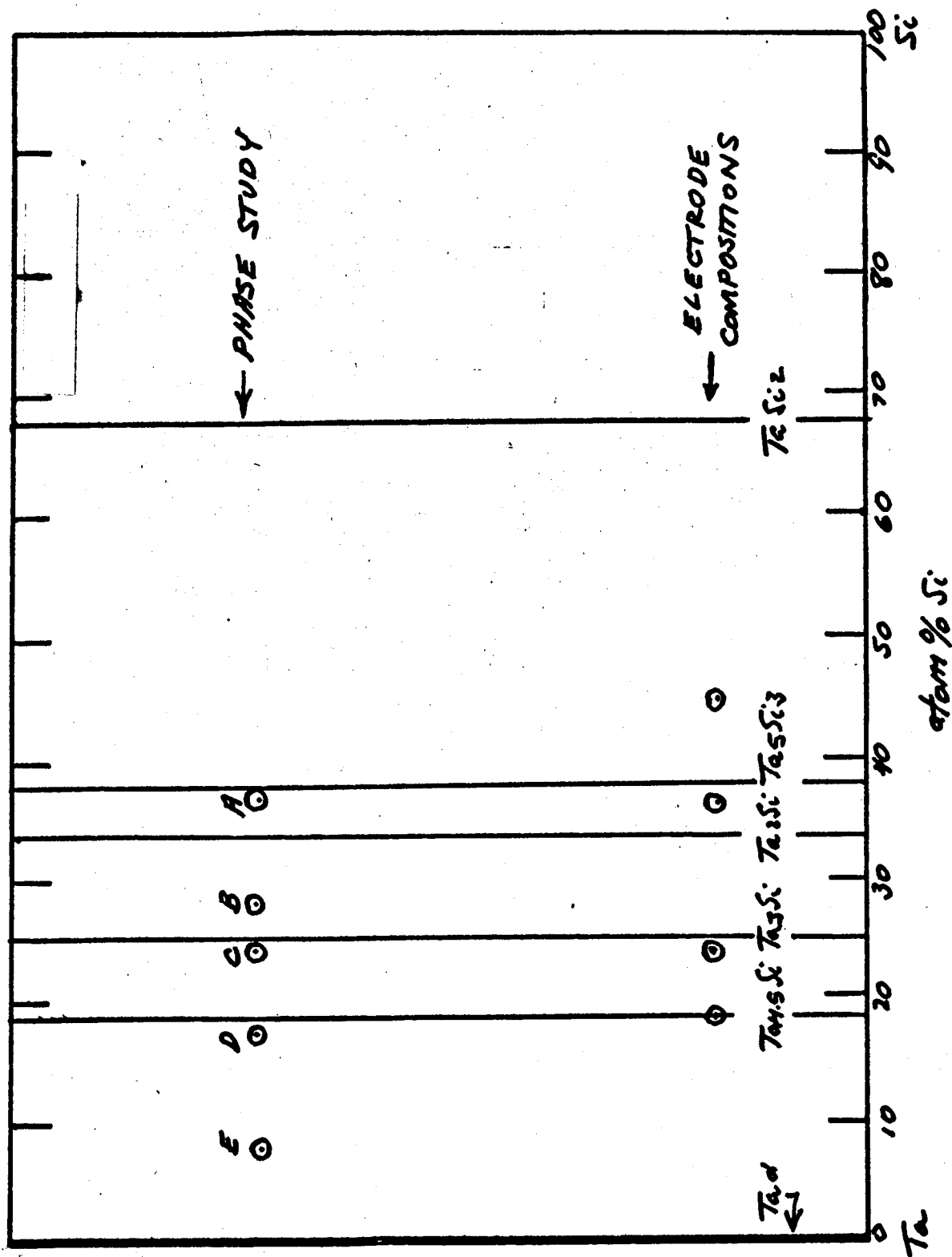


FIGURE 2. ELECTRODES AND SPECIMENS PREPARED FOR X-RAY ANALYSIS

Figure 3
Tantalum-Silicon System²²

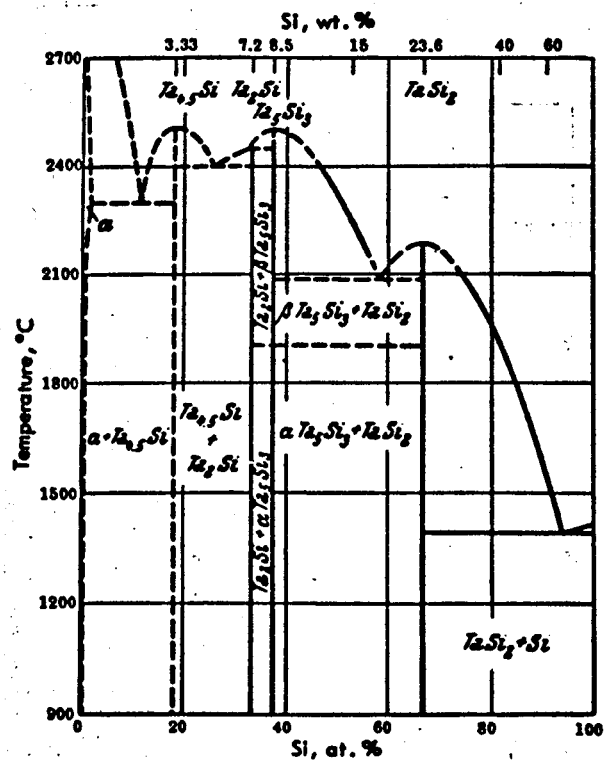


Figure 4
Titanium-Silicon System²²

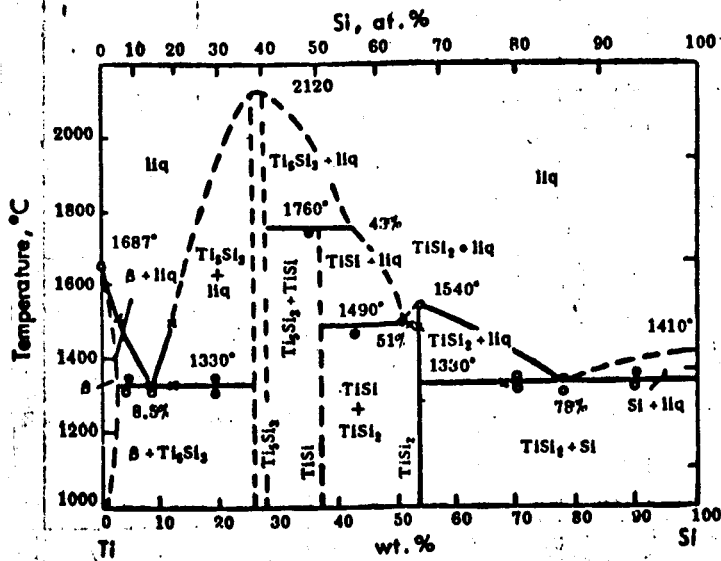


Figure 5

TaSi₂-TiSi₂ System²³

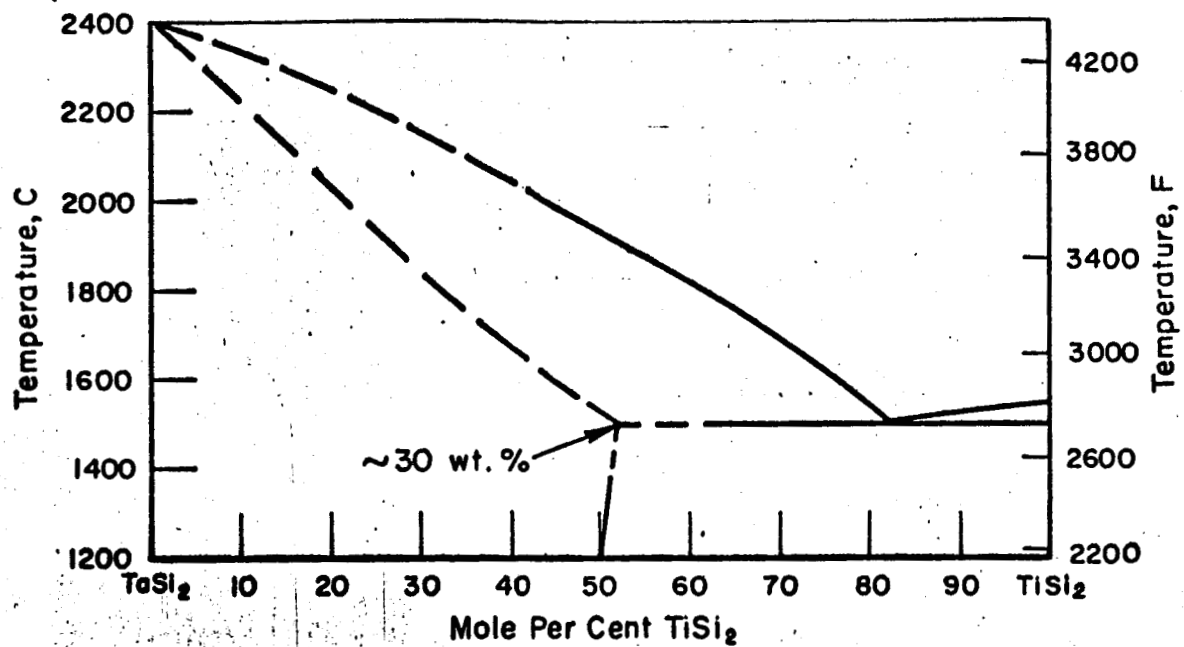


Figure 6

TiO₂-SiO₂ System²⁴

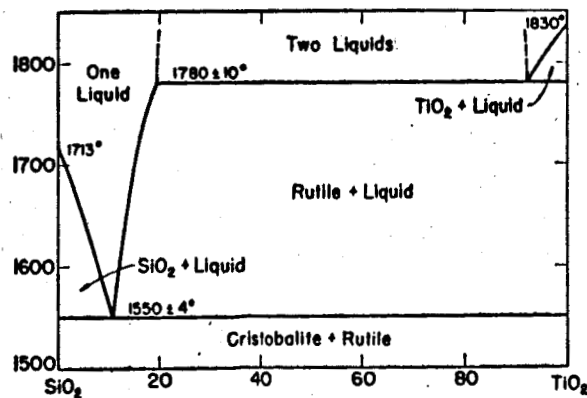


Figure 7

Thermodynamic Data for Marker Materials

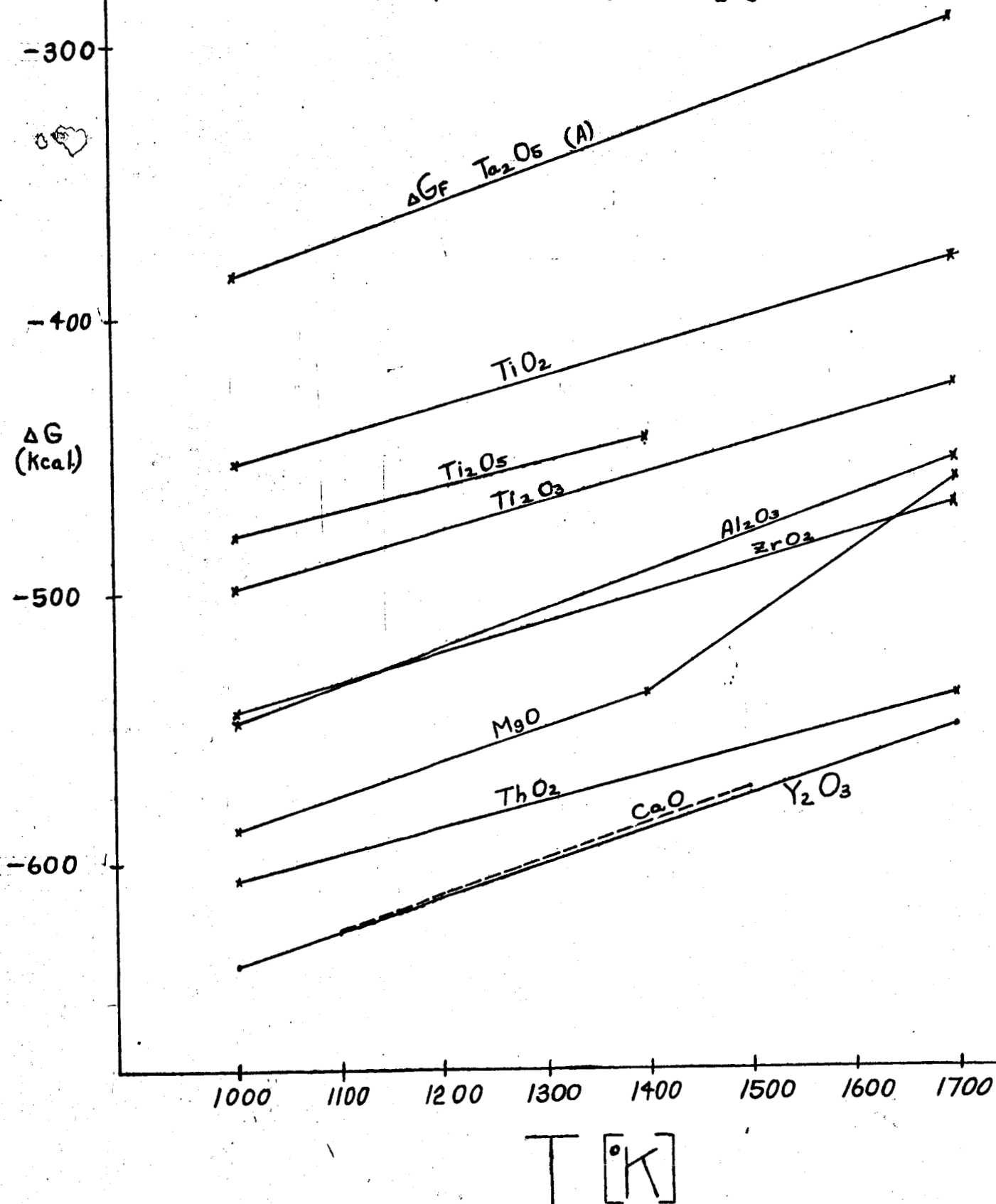
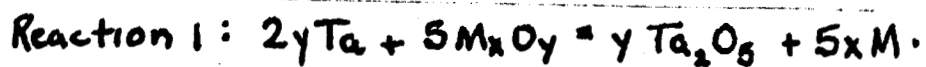
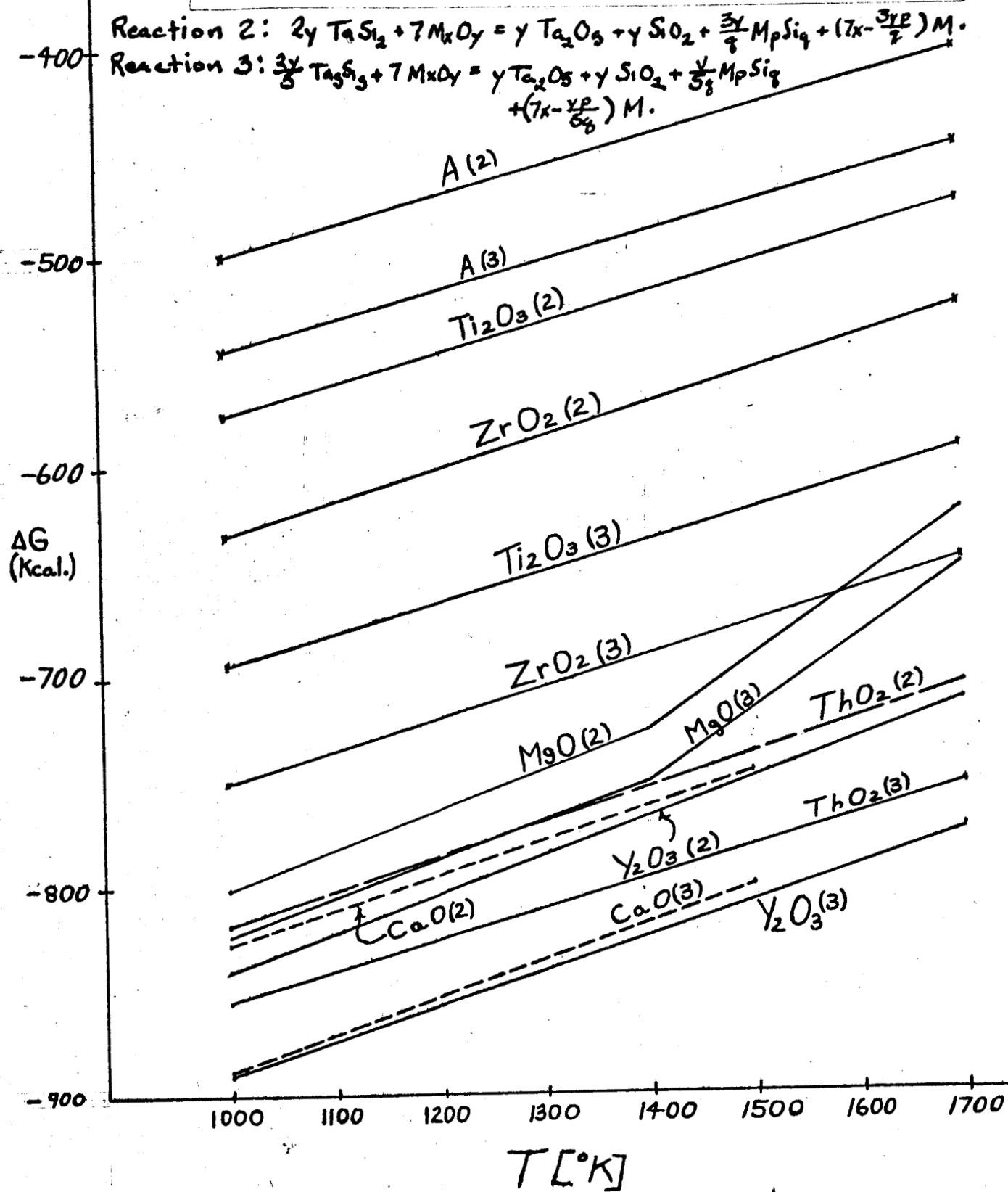


Figure 8

Thermodynamic Data for Marker Materials



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